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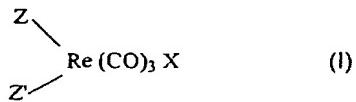
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(54) Title: RHENIUM COMPOUNDS



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(57) **Abstract:** An organic electroluminescent device is described which comprises a compound having a skeleton of the formula (I): which skeleton can comprise one or more additional aromatic rings, wherein each of Z and Z', which may be the same or different, represents a nitrogen-containing aromatic ring such that the Z and Z' rings either together form a conjugated system, optionally with one or more additional aromatic rings, or at least one of Z and Z' form a conjugated system with one or more additional aromatic rings to which Z and Z' are attached, with the proviso that, (a) when the two said rings are pyridyl rings and are connected to one another ortho to the nitrogen atoms then (i) at least one said ring is substituted by at least one electron withdrawing substituent which is a hydrocarbon aryl group or (ii) at least one said ring is fused to another aromatic ring to which the other pyridyl ring is not fused or (iii) the two said rings together form a phenanthroline ring system which is substituted by at least one electron withdrawing substituent which is in the 2, 4, 5, 6, 7 or 9 position, or (b) the two said rings are such that either (i) at least one of them contains at least one further nitrogen atom or (ii) they are fused to another aromatic ring which contains at least one nitrogen atom, and X represents an anionic or neutral coligand.

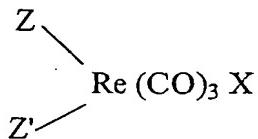
## RHENIUM COMPOUNDS

This invention relates to rhenium compounds and, in particular, rhenium compounds which are useful as emitting materials in electroluminescent (EL) devices.

5       Numerous metal complexes have been proposed as emitting materials in EL devices. One of the difficulties is that although many such compounds show promise when tested in solution, they are not efficient emitters in the solid state. In addition, although there are many candidates for use as emitters at the green portion of the spectrum, including green phosphorescent materials such as iridium tris (phenylpyridine), there is a marked lack of emitters towards the red end of the 10 spectrum. Only a few red phosphorescent materials have been demonstrated for use in EL devices. Red emitting 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum has a relatively long decay lifetime and in many ways is too deep a red colour which reduces useful efficiency. Some red emitting Ir compounds such as 15 iridium (III) bis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)(acetylacetone) are also known but they have not yet been proved to have sufficient lifetime in devices and there is still scope for efficiency improvements. There is, therefore, a need for efficient emitters which emit red light with good colour purity, particularly for use in full colour displays and that have good efficiency in EL devices. It is therefore an 20 object of the invention to provide materials emitting towards the red region of the spectrum, particularly materials with good red emission that are suitable for use in full colour displays, and that have good efficiency and short luminescence decay lifetimes.

It has been found, according to the present invention, that certain rhenium 25 complexes possessing three co-ordinating carbonyl ligands together with a bidentate, diimine-type ligand can be used in EL devices which emit generally in the yellow to red region of the spectrum. According to the present invention there is provided an electroluminescent device which comprises a compound having a skeleton of the formula:

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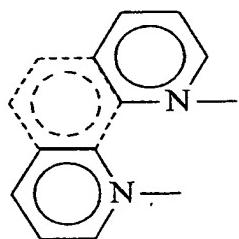


- which skeleton can comprise one or more additional aromatic rings, wherein each of Z and Z', which may be the same or different, represents a nitrogen-containing aromatic ring such that the Z and Z' rings either together form a conjugated system, optionally with one or more additional aromatic rings, or at least one of Z and Z'
- 5      form a conjugated system with one or more additional aromatic rings to which Z and Z' is attached, with the proviso that, (a) when the two said rings are pyridyl rings and are connected to one another ortho to the nitrogen atoms then (i) at least one said ring is substituted by at least one electron withdrawing substituent which is a hydrocarbon aryl group or (ii) at least one said ring is fused to another aromatic ring to which the
- 10     other pyridyl ring is not fused or (iii) the two said rings together form a phenanthroline ring system which is substituted by at least one electron with-drawing substituent which is in the 2, 4, 5, 6, 7 or 9 position, or (b) the two said rings are such that either (i) at least one of them contains at least one further nitrogen atom or (ii) they are fused to another aromatic ring which contains at least one nitrogen atom, and
- 15     X represents an anionic or neutral coligand. The EL device results from the compounds of the invention, such as 4,7-diphenyl- 2,9-dimethyl-1,10-phenanthroline (compound 1), are red shifted and significantly more efficient than the prior art EL results from the Re compound shown in Syn. Met. 118, 2001, 175-179 which does not posses an electron withdrawing substituent.
- 20     The compounds where the two said rings are such that either (i) at least one of them, and preferably only one of them, contains at least one further nitrogen atom or (ii) they are fused to another aromatic ring which contains at least one nitrogen atom i.e. such compounds containing at least 3, for example 4, ring nitrogen atoms are

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novel apart from 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine and 3, 5, 6-tri (2-pyridyl)-1, 2, 4-triazine, when X is chlorine and form another aspect of the present invention. When we say "fused to another aromatic ring which contains at least one nitrogen atom" we mean directly fused. Typically the nitrogen-containing rings are 6-membered, especially when they contain 2 or more hetero atoms. If the ring is 5 membered and possesses more than one heteroatom this second heteroatom is preferably nitrogen. Indeed in one embodiment all the heteroatoms are nitrogen. It is preferred that when the nitrogen-containing ring contains 2 or more nitrogen atoms it is a 6-membered ring. Preferably the ring system has the structure:

10

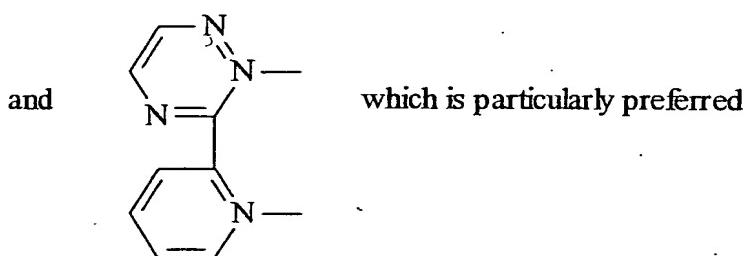
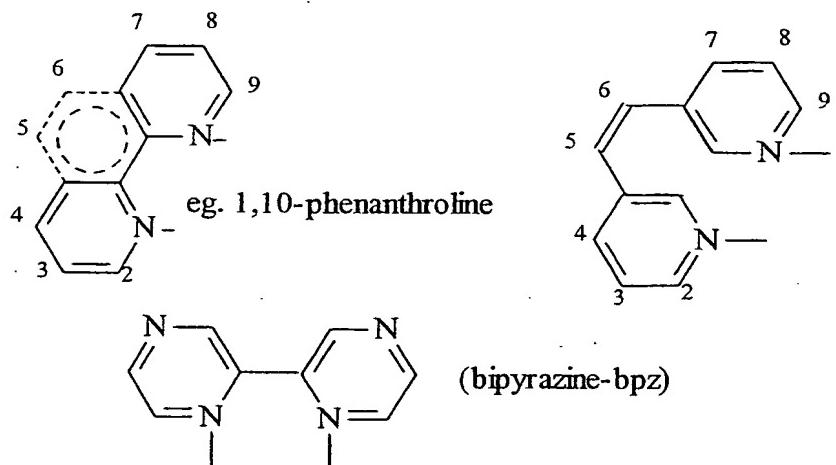


The dotted lines represent optional bonds. Generally the system will be conjugated, for example by a single bond connecting the two pyridyl rings, by a third aromatic ring or by a -C' = C'- link.

If the nitrogen-containing rings are pyridyl rings then they are typically linked together via their ortho carbon atoms or connected by a -C'=C'- link via carbon atoms meta to the nitrogen atoms. Alternatively they can be fused to a benzene ring to form a phenanthroline ring or to a nitrogen-containing aromatic ring. If one of the nitrogen-containing rings is not a pyridyl ring then it can contain one or more additional nitrogen atoms.

20 Thus typical ring systems include the following:

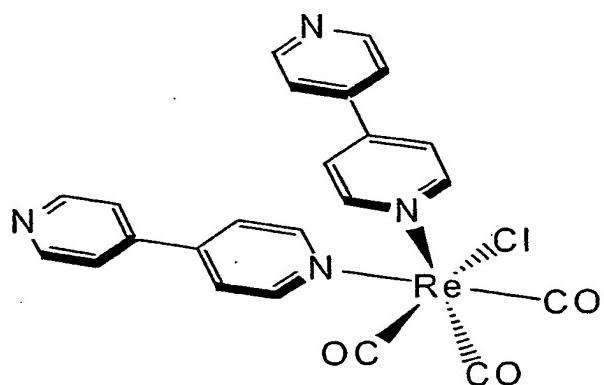
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as well as two unconnected N

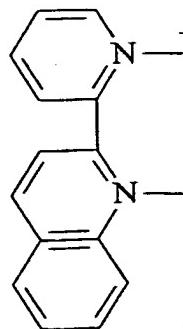
rings, as  
in  $[\text{Re}(\text{CO})_3(4,4'\text{-bipyridyl})_2\text{Cl}]$  as shown below

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A common feature of the compounds of the invention is that the conjugation of the Z-Z' ligand system has been extended or modified to produce the red shift and increase in luminous efficiency.

- 5 When the ring system is bipyridyl or phenanthroline, it is necessary for at least one ring to be substituted by an electron withdrawing substituent unless one of the rings is fused to an aromatic ring as in:



- Additionally when the ring system is bipyridyl the electron withdrawing substituent is a hydrocarbon aryl group (which can be substituted) and when the ring system is a phenanthroline ring system the electron withdrawing substituent is in the 2, 4, 5, 6, 7 or 9 position.

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Given the relatively low sensitivity of the HOMO energy to changes to the diimine ligand the emission energy of Re(I) complexes is, broadly speaking, proportional to the reduction potential of the ligand. In general, Re(I) complexes emit in the yellow-green region of the spectrum. The colour of this emission can  
5 therefore be red shifted by lowering the LUMO energy i.e. by making the ligand reduction potential more positive. Such a change can be made either by changing the ligand itself or by introducing electron withdrawing substituents. In particular it is preferred that there are two substituents on at least one of the rings and at least one of these substituents is an electron withdrawing group. The presence of two substituents  
10 allows greater control over the energy levels, can improve the processing properties, and in some cases, such as when the substituents are phenyl groups, can increase the luminescence quantum yield.

Thus for all the ring systems which can be used the presence of an electron withdrawing substituent is generally beneficial. The definition of an electron  
15 withdrawing group is the tendency for an atom or group of atoms to attract electron density from the ligand towards itself relative to a hydrogen atom such that atoms or groups of atoms with a greater tendency to attract electron density towards themselves than a hydrogen atom are known as electron withdrawing groups.

Examples of electron withdrawing groups include nitro; nitroso; cyano; thiocyanato;  
20 cyanato; aldehyde; ether; carboxylic acid; azide; aryl, such as phenyl; heteroaryl, such as pyridyl, e.g. 4-pyridyl, pyrazole, furan, thiophene; halogen, e.g. fluorine, chlorine, bromine, iodine; ester, such as alkoxycarbonyl, e.g. ethoxycarbonyl; chalcogenoester, such as alkyl chalcogenoester, e.g.  $\text{CH}_3\text{EO}_2$ , or aryl chalcogenoester, e.g.  $\text{PhEO}_2$  (where E can be S, Se or Te); fluoroalkyl, such as  
25 trifluoroalkyl, e.g. trifluoromethyl and pentafluoroethyl; hypophosphate, e.g.  $\text{H}_2\text{PO}_3^-$ ; sulfonate, such as aryl sulfonate, e.g.  $p\text{-CH}_3\text{PhSO}_3^-$ ; acyl halide, e.g.  $\text{COCl}$ ; amide, such as  $\text{CONH}_2$ ,  $\text{CONHR}$ ,  $\text{CONR}_2$  (where R can in turn be hydrogen or any organic group such as alkyl or aryl); substituted N-oxide such as NOR, e.g.  $\text{NOCH}_3$ ; hydrazide, such as  $\text{NR-NR}'_2$  (where R and R' can in turn be hydrogen or any organic  
30 group such as alkyl or aryl); quaternary amine, such as tetralkylammonium, e.g.

Et<sub>4</sub>N; silyl, such as SiR<sub>3</sub> (where R can in turn be hydrogen or any organic group such as alkyl or aryl); substituted, bivalent chalcogenide, such as alkyl seleno or sulfonyl groups, e.g. CH<sub>3</sub>Se, CF<sub>3</sub>S as well as trifluoromethylphenyl, pentafluoroethylphenyl and pentafluorophenyl. Of course all of these electron withdrawing groups can be  
5 substituted.

In some instances the electron withdrawing group or groups may be so strong such that the shift goes beyond the red region; examples of such groups include NO<sub>2</sub> and oxadiazole. In such circumstances it may be desirable to include an electron  
10 donating substituent as well; suitable such substituents include alkyl such as methyl and t-butyl, alkoxy such as methoxy, amino or substituted amino such as diethylamino, as well as amido, typically aliphatic acyl amido such as acetamido. The alkyl groups which may form part of, or be, a substituent typically have 1 to 6, for example 1 to 4, carbon atoms.

Phenyl substituents, in particular, have been found to be beneficial since not  
15 only do they shift the emission towards the red position region but their presence can also increase the luminescence quantum yield. A phenyl group substituted by one (or more) fluorine or fluorine-containing groups, for example trifluoromethyl, has a stronger electron withdrawing effect than a phenyl group and shifts the emission further to the red region

20 Substituents can be present on any position of the rings. However, it is preferred that the electron withdrawing substituent is not meta to the N-Re bond, i.e. is not in the 3 position for pyridyl and phenanthroline ligands, because the electronic effect of an electron withdrawing group at the meta position is much less than it would be in the ortho or para positions, and the intention in this invention is that the  
25 electron withdrawing group is present to modify the LUMO level of the diimine ligand to control the emission colour. Preferably substituents are para to the ring nitrogen atom i.e. in the 4 position for bipyridyl. For phenanthroline typical positions are 2,4,5,6,7 and 9 with the 4 and 7, 5 and 6, or 2 and 9, pairs being generally preferred. For the preferred triazine-pyridyl system the substituents are  
30 preferably in the triazine ring; a particularly preferred diimine system is 2-(2-

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pyridyl-4,5-diphenyl-triazine-) (dppt).

When the Z and Z' rings are the same it is preferred that there is an electron withdrawing group on both Z and Z'. It is further preferred that when the Z and Z' rings are the same there is the same type of substituent at the same relative positions  
5 on each.

As indicated above, the coligand X is neutral or anionic (if X is neutral then a non-coordinating counter anion is required to form a stable complex). A wide variety of coligands can be used including nitrate, nitrite, perchlorate, iodate, bromate, chlorate, chlorite, hypochlorite, hypobromite, bicarbonate,  
10 trifluoromethylsulfonate, hydride, dihydrogen phosphate, hydrogen sulfate; also hydrocarbonyl groups such as phenyl, alkyl and substituted alkyl eg aralkyl such as benzyl; also anions from organic acids such as acetate and formate; also sulfonates including alkyl and aryl sulfonates; also cyanide, cyanate, thiocyanate, hydroxide and amide; also inorganic anions such as permanganate; also alkyl and aryl alcohols,  
15 thiols and amines; also heteroaromatic groups such as pyrroles, imidazoles, pyrazoles and carbenes; also borates such as trispyrazolyl borates. However X is preferably a halide including chloride, fluoride, bromide and iodide. It has surprisingly been found that in the solid state the difference in luminescence efficiency between complexes having a halide ligand rather than a neutral ligand is  
20 nowhere near as great as solution data would suggest.

Varying the halide from chloride to bromide to iodide leads to only slight shifts in the HOMO and LUMO energy levels, but varying the halide ion affects both the lifetime and the quantum efficiency of the emission. Qualitative measurements on complexes 3, 4 and 9 - see below (which all have X =Br) and complex 13 (which  
25 has X=I) support the conclusion that the heavier halides give more efficient emissions.

A further advantage of halide-based over neutral-ligand based complexes is long-term photostability of the complexes. In ambient conditions under a UV lamp halide based complexes have exhibited no observable decomposition whereas a  
30 sample of 7 (see below), which contains a pyridyl coordinating ligand and a non-

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coordinating perchlorate anion, in the solid state showed marked photodecomposition in its spectra on standing in air for several months. Enhanced photostability should lead to intrinsically stable materials for electroluminescent devices. Photostability also provides a route to designing photopolymerisable compounds for  
5 photopatternable electroluminescent devices. Thus if they possess a radical, cationic or anionic polymerisable group, especially a photopolymerisable group as a substituent, then the compounds can be polymerised to form a polymer possessing pendant luminescent Re-containing ring systems. Examples of suitable photopolymerisable substituent groups are olefin groups such as an acrylate  
10 derivative or vinyl, or strained ring systems such as an oxetane or epoxide, or other known one or two-component systems.

Apart from forming polymers, the rhenium complexes can also form part of dendrimers such as those of the type disclosed in WO99/21935. Thus the complex possesses one or more substituents, which forms part of a dendritic structure such  
15 that the molecule is a dendrimer. The use of suitable dendritic branches can give the molecules good solubility and film forming properties, which are useful if solution processing techniques are to be used in the manufacture of the EL device. The dendrimer can comprise at least one co-ordinating group which is not dendritic. In a preferred embodiment a dendrimer of the present invention will comprise one  
20 coordinating group which is dendritic and 3 CO ligands and an X ligand bound to the Re ion. The dendrite(s) is/are preferably bound to the diimine-type ligand and the CO and X ligands are not dendritic. Such dendrimers can be prepared using the techniques disclosed in WO 99/21935 to which reference should be made for further details.

25 The compounds used in the present invention can generally be prepared by reacting the desired diimine-type ligand with a rhenium complex of the formula Re(CO)<sub>5</sub>X. Typically they can be reacted by using roughly equimolar amounts, with heating, typically under reflux in a nonpolar organic solvent such as toluene or a polar solvent such as methanol or chloroform, in an inert atmosphere, for example  
30 argon. Generally the desired complex can be obtained as a precipitate on cooling.

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The precipitate can be washed and dried and, if desired, further purified by vacuum sublimation.

In its simplest form, an organic light emitting or electroluminescent device of this invention can be formed from a light emitting layer sandwiched between two

5 electrodes at least one of which must be transparent to the emitted light. Typically, the device can be formed from a transparent substrate layer, a transparent electrode, a layer of light emitting material, and a second electrode. In a conventional structure the transparent electrode is the anode and the final electrode is the cathode. The transparent substrate is typically made of glass, but could be a transparent plastic

10 such as PET. The transparent anode is preferably made from indium tin oxide (ITO), although other similar materials as well as conducting polymers such as PANI (polyaniline) may also be used. The cathode is generally made of a low work function metal or alloy such as Al, Ca, Mg, Li, or MgAg. As is well known, other layers may also be present, including a hole transporting material and / or an electron

15 transporting material. In an alternative configuration, the substrate may be an opaque material such as silicon, and the light is emitted through the opposing electrode.

In one embodiment, the complexes of the present invention form a light emitting layer between the electrodes. A light emitting device can be formed with a single layer containing one or more compounds of this invention, optionally mixed

20 with one or more other molecular, dendritic or polymeric species between the electrodes, but other layers may also be present. In particular there may be a hole transporting layer(s) between the anode and the light emitting layer and / or an electron transporting material between the light emitting layer and the cathode.

Typical hole transporting materials include triarylamines such as TPD or  $\alpha$ -NPD, or

25 PEDOT:PSS. It can be beneficial to include a hole blocking/electron transporting layer between the emissive layer and the cathode. Examples of hole blocking materials include 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and 2,2',2"- (1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI). Examples of electron transporting materials include oxadiazoles or aluminium *tris*(8-hydroxyquinolate). In addition there may be an electron injecting layer deposited before the cathode,

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suitable materials include LiF. Addition of suitable hole or electron transporting layers can improve the efficiency and/or lifetime of the device.

The layer comprising the compound of the present invention may consist of the compound or the compound can be added into a host forming a blend. Typical host materials include a phosphorescent matrix such as a benzophenone or an acetophenone derivative, for example 1,1,1-triphenylacetophenone or 4,4'-dimethoxybenzophenone, or a lanthanide complex whose ligand has a higher triplet energy than that of the complex of this invention, or an oxadiazole such as 1,3-bis[5-(4-tert-butylphenyl)-[1,3,4]oxadiazol-2-yl]-benzene or a carbazole such as 4,4'-bis(carbazol-4-yl) biphenyl (CBP), or 4,4',4''-tri(N-carbazolyl)triphenylamine (TCTA).

Devices containing the compounds of the invention can be prepared in a conventional manner. In a preferred embodiment the compounds are deposited on the substrate by physical vapour deposition (evaporation under reduced pressure). In another embodiment the compounds or blend of compounds are deposited from solution, for example by spin-coating, ink-jet printing, or other solution processing techniques.

The following Examples further illustrate the present invention.

The following compounds were prepared:

20

### Examples

The general synthesis of the [Re(i)(CO)<sub>3</sub>(L)X]-type complexes (X = Cl, Br) is as follows:

A stirred suspension of equimolar amounts of [Re(CO)<sub>5</sub>X] and the diimine-type ligand in toluene was heated at reflux under an Ar atmosphere for 2 hrs. Typically, the suspension changed colour and became a solution within 5 - 10 mins. On cooling a precipitate formed which was collected by filtration, washed with pentane and dried under vacuum. The complexes were further purified by vacuum sublimation. Chemical yields were between 70 and 90%.

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### Example 1

[Re(CO)<sub>3</sub>(2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>phen)Cl] (**1**)

The reaction of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with Re(CO)<sub>5</sub>Cl gave a yellow powder. The product was purified by sublimation at 265 °C at 9 · 10<sup>-6</sup> mbar.

- 5 Found C: 51.82, H: 2.63, N: 4.09; C<sub>29</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>3</sub>Re requires C: 52.29, H: 3.03, N: 4.21%. δ<sub>H</sub> (CDCl<sub>3</sub>) 7.87 (2 H, s), 7.70 (2 H, s), 7.60–7.40 (10 H, m), 3.40 (6 H, s). IR: (nujol) ν<sub>CO</sub> (cm<sup>-1</sup>) 2013, 1915, 1879, 1862. Emission spectra: CH<sub>2</sub>Cl<sub>2</sub> (λ<sub>ex</sub> = 330 nm) λ<sub>max</sub> = 576 nm, CIE: 0.425, 0.516; powder (λ<sub>ex</sub> = 435 nm) λ<sub>max</sub> = 532 nm, CIE: 0.338, 0.620.

10

### Example 2

[Re(CO)<sub>3</sub>(dppt)Cl] (**2**)

The reaction of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (dppt) with Re(CO)<sub>5</sub>Cl gave an orange powder. The product was purified by sublimation at 280 °C at 1 · 10<sup>-6</sup>

- 15 mbar. Found C: 44.83, H: 2.30, N: 9.12; C<sub>23</sub>H<sub>14</sub>ClN<sub>4</sub>O<sub>3</sub>Re requires C: 44.84, H: 2.29, N: 9.09%. δ<sub>H</sub> (CDCl<sub>3</sub>) 9.04 (1 H, d), 8.70 (1 H, d), 8.11 (1 H, t), 7.70–7.00 (11 H, m). Emission spectrum: powder (λ<sub>ex</sub> = 435 nm) λ<sub>max</sub> = 617 nm, CIE: 0.632, 0.366.

### Example 3

- 20 [Re(CO)<sub>3</sub>(2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>phen)Br] (**3**)

The reaction of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with Re(CO)<sub>5</sub>Br gave a yellow powder. The product was purified by sublimation at 260 °C at 5 · 10<sup>-7</sup> mbar.

Found C: 51.53, H: 3.95, N: 3.28; C<sub>29</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>3</sub>Re requires C: 49.02, H: 2.84, N: 3.94%.

25

### Example 4

[Re(CO)<sub>3</sub>(dppt)Br] (**4**)

The reaction of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (dppt) with Re(CO)<sub>5</sub>Br gave an orange powder. δ<sub>H</sub> (CDCl<sub>3</sub>) 9.12 (1 H, d), 8.76 (1 H, d), 8.17 (1 H, t), 7.80–7.10

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(11 H, m). Emission spectra: CHCl<sub>3</sub>, ( $\lambda_{\text{ex}} = 519$  nm)  $\lambda_{\text{max}} = 624$  nm, CIE: 0.655, 0.345; powder ( $\lambda_{\text{ex}} = 440$  nm)  $\lambda_{\text{max}} = 619$  nm, CIE: 0.600, 0.395.

**Example 5**

5 [Re(CO)<sub>3</sub>(2,4,7,9-Ph<sub>4</sub>phen)Cl] (5)  
2,9,4,7-tetraphenyl-1,10-phenanthroline was prepared from phenyllithium and 4,7-diphenyl-1,10-phenanthroline as described by Sauvage *et al.* (*Tet. Lett.*, 23, 50, 1982, 5291). Found C: 89.30, H: 4.22, N: 5.53; C<sub>36</sub>H<sub>24</sub>N<sub>2</sub> requires C: 89.23, H: 4.99, N: 5.78%. δ<sub>H</sub> (CDCl<sub>3</sub>) 8.52 (4 H, d), 8.09 (2 H, s), 7.81 (2 H, s), 7.65-7.55 (16 H, m). EI  
10 MS 484.1 (M<sup>+</sup>).

The reaction of 2,9,4,7-tetraphenyl-1,10-phenanthroline with Re(CO)<sub>5</sub>Cl gave an orange powder. The product was purified by sublimation at 275 °C at 3 · 10<sup>-6</sup> mbar. Found C: 60.22, H: 3.05, N: 3.51; C<sub>39</sub>H<sub>24</sub>ClN<sub>2</sub>O<sub>3</sub>Re requires C: 59.27, H: 3.06, N: 3.54%. δ<sub>H</sub> (CDCl<sub>3</sub>) 8.05 (2 H, s), 7.95 (2 H, s), 7.93-7.87 (4 H, m), 7.65-7.45 (18 H, m). IR: (solid) ν<sub>CO</sub> (cm<sup>-1</sup>) 2018, 1917, 1869. EI MS 790.1 (M<sup>+</sup>). Emission spectra: CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{ex}} = 450$  nm)  $\lambda_{\text{max}} = 591$  nm, CIE: 0.545, 0.452; powder ( $\lambda_{\text{ex}} = 475$  nm)  $\lambda_{\text{max}} = 592$  nm, CIE: 0.567, 0.432.

20 **Example 6** (Comparative example)

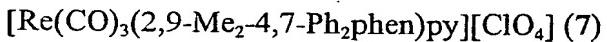
[Re(CO)<sub>3</sub>(2,4,7,9-Me<sub>4</sub>phen)(4,4'bpy)][(CF<sub>3</sub>SO<sub>3</sub>)] (6)

This complex was prepared as described by Guarr *et al.* (*Inorg. Chem.*, 1992, 4346). Emission spectrum:  $\lambda_{\text{max}} = 527$  nm,  $\phi = 0.57$  (MeCN, 298 K). The yellow powder was sublimed at 300 °C at 1 · 10<sup>-6</sup> mbar. <sup>1</sup>H nmr and elemental analysis of the 25 sublimation product is consistent with the formulation [Re(CO)<sub>3</sub>(Me<sub>4</sub>phen)][(CF<sub>3</sub>SO<sub>3</sub>)] where the 4,4'bpy ligand has been lost.

The emission wavelength (in solution) of this comparative example is undesirably blue shifted relative to the emission wavelengths of the compounds of the invention.

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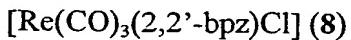
**Example 7**



This complex was prepared as described by DeGraff *et al.* (*Inorg. Chem.*, 1993, 5629). Emission spectrum:  $\lambda_{\text{em}} = 555$  nm,  $\phi = 0.32$  (CH<sub>2</sub>Cl<sub>2</sub>, 298 K).

5

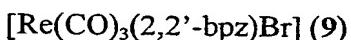
**Example 8**



2,2'-Bipyrazine was prepared as described by Lever *et al.* (*Inorg. Chem.*, 1982, 2276). The reaction of 2,2'-bipyrazine with Re(CO)<sub>5</sub>Cl gave an orange powder.

- 10 Found C: 28.62, H: 1.27, N: 12.18; C<sub>11</sub>H<sub>6</sub>ClN<sub>4</sub>O<sub>3</sub>Re requires C: 28.48, H: 1.30, N: 12.08%.  $\delta_H$  (CDCl<sub>3</sub>) 10.15 (2 H, s), 9.15 (2 H, d), 9.00 (2 H, d). IR: (nujol)  $\nu_{\text{CO}}$  (cm<sup>-1</sup>) 2022, 1938, 1911. Emission spectrum: powder ( $\lambda_{\text{ex}} = 400$  nm)  $\lambda_{\text{max}} = 635$  nm, CIE: 0.674, 0.326.

- 15 **Example 9**



2,2'-Bipyrazine was prepared as described by Lever *et al.* (*Inorg. Chem.*, 1982, 2276). The reaction of 2,2'-bipyrazine with Re(CO)<sub>5</sub>Br gave an orange powder.

- Found C: 26.16, H: 1.92, N: 11.24; C<sub>11</sub>H<sub>6</sub>BrN<sub>4</sub>O<sub>3</sub>Re requires C: 25.99, H: 1.19, N: 11.02%.  $\delta_H$  (CDCl<sub>3</sub>) 9.69 (2 H, s), 9.06 (2 H, d), 8.87 (2 H, d). Emission spectrum: powder ( $\lambda_{\text{ex}} = 450$  nm)  $\lambda_{\text{max}} = 641$  nm, CIE: 0.670, 0.329.

**Example 10**

- 25 [Re(CO)<sub>3</sub>{2,9-(4-CF<sub>3</sub>Ph)<sub>2</sub>-4,7-Ph<sub>2</sub>phen}Cl] (10)

The novel ligand, 2,9-bis(4-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline, was prepared from 4-bromobenzotrifluoride and 4,7-diphenyl-1,10-phenanthroline by the method of Sauvage *et al.* (*Tet. Lett.*, 23, 50, 1982, 5291).  $\delta_H$

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(CDCl<sub>3</sub>) 8.59 (4 H, d), 8.11 (2 H, s), 7.95–7.80 (8 H, m), 7.70–7.40 (12 H, m), δ<sub>F</sub> (CDCl<sub>3</sub>) –63.4 (s).

The reaction of 2,9-bis(4-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline with Re(CO)<sub>5</sub>Cl gave an orange powder. The product was purified by sublimation at 275 °C at 5 × 10<sup>–6</sup> mbar. δ<sub>H</sub> (CDCl<sub>3</sub>) 8.11 (2 H, s), 8.00–7.80 (10 H, m), 7.70–7.50 (10 H, m), δ<sub>F</sub> (CDCl<sub>3</sub>) –63.4 (s), IR: (solid) ν<sub>CO</sub> (cm<sup>–1</sup>) 2028, 1936, 1877. Emission spectra: CH<sub>2</sub>Cl<sub>2</sub> (λ<sub>ex</sub> = 451 nm) λ<sub>max</sub> = 596 nm, CIE: 0.554, 0.442; powder (λ<sub>ex</sub> = 468 nm) λ<sub>max</sub> = 585 nm, CIE: 0.535, 0.461.

10

#### Example 11

[Re(CO)<sub>3</sub>{2,9-(3-CF<sub>3</sub>Ph)<sub>2</sub>-4,7-Ph<sub>2</sub>phen}Cl] (11)

15 The novel ligand, 2,9-bis(3-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline, was prepared from 3-bromobenzotrifluoride and 4,7-diphenyl-1,10-phenanthroline by the method of Sauvage *et al.* (*Tet. Lett.*, 23, 50, 1982, 5291). δ<sub>H</sub> (CDCl<sub>3</sub>) 8.83 (2 H, br s), 8.68 (2 H, br d), 8.11 (2 H, s), 7.86 (2 H, s), 7.80–7.65 (4 H, m), 7.65–7.50 (10 H, m), δ<sub>F</sub> (CDCl<sub>3</sub>) –63.1 (s).

20

The reaction of 2,9-bis(3-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline with Re(CO)<sub>5</sub>Cl gave an orange powder. The product was purified by sublimation at 265 °C at 5 × 10<sup>–6</sup> mbar. Found C: 53.22, H: 2.38, N: 3.04; C<sub>41</sub>H<sub>22</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>3</sub>Re requires C: 53.16, H: 2.39, N: 3.02%. δ<sub>H</sub> (CDCl<sub>3</sub>) 8.11 (2 H, s), 8.10–7.65 (10 H, m), 7.58 (10 H, br s), δ<sub>F</sub> (CDCl<sub>3</sub>) –63.1 (s). IR: (solid) ν<sub>CO</sub> (cm<sup>–1</sup>) 2020, 1926, 1892.

Emission spectra: CH<sub>2</sub>Cl<sub>2</sub> (λ<sub>ex</sub> = 396 nm) λ<sub>max</sub> = 635 nm, CIE: 0.626, 0.373; thin film (λ<sub>ex</sub> = 396 nm) λ<sub>max</sub> = 610 nm, CIE: 0.569, 0.429.

#### Example 12

30

[Re(CO)<sub>3</sub>(2,2'-biq)Cl] (12)

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The reaction of 2,2'-biquinoline (2,2'-biq) with Re(CO)<sub>5</sub>Cl gave a red powder as described by Wrighton *et al.* (*J. Amer. Chem. Soc.*, 1974, 998). δ<sub>H</sub> (CDCl<sub>3</sub>) 8.95 (2 H, d), 8.58 (2 H, d), 8.39 (2 H, d), 8.10–7.90 (4 H, m), 7.68 (2 H, tr).

5 **Example 13**

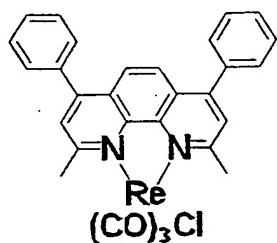
[Re(CO)<sub>3</sub>(2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>phen)I] (13)

One molar equivalent of silver triflate was added to a suspension of **1** in acetone. The mixture was heated at reflux under Ar for 2 hrs. The yellow/orange mixture was cooled and the white solid removed by filtration. The solvent from the filtrate was

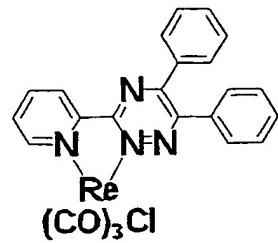
10 removed under vacuum and the residue redissolved in toluene. 10 molar equivalents of sodium iodide was added to the solution and the mixture heated at reflux for 8.5 hrs. The mixture was filtered and the solvent from the filtrate removed under vacuum. The product was recrystallised from dichloromethane / pentane to give a green powder in 66% yield. The product was purified by sublimation at 260 °C at 2

15 10<sup>-6</sup> mbar. Found C: 45.80, H: 1.89, N: 3.87; C<sub>29</sub>H<sub>20</sub>IN<sub>2</sub>O<sub>3</sub>Re requires C: 45.98, H: 2.66, N: 3.70%. δ<sub>H</sub> (CDCl<sub>3</sub>) 7.88 (2 H, s), 7.71 (2 H, s), 7.60–7.40 (10 H, m), 3.40 (6 H, s). Emission spectra: CH<sub>2</sub>Cl<sub>2</sub> (λ<sub>ex</sub> = 313 nm) λ<sub>max</sub> = 569 nm, CIE: 0.463, 0.525; powder (λ<sub>ex</sub> = 400 nm) λ<sub>max</sub> = 527 nm, CIE: 0.293, 0.636.

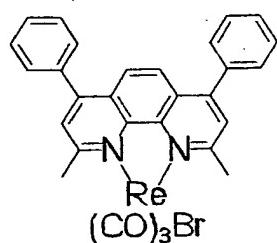
-17-



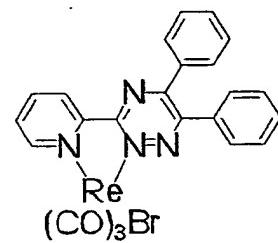
(1)



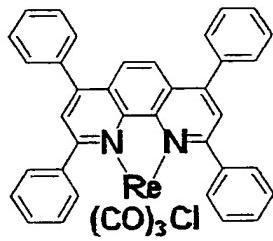
(2)



(3)

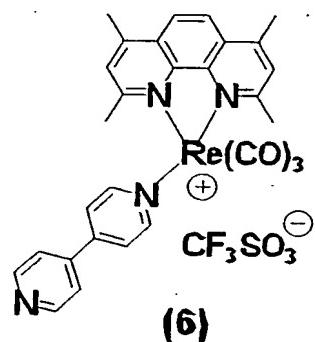


(4)

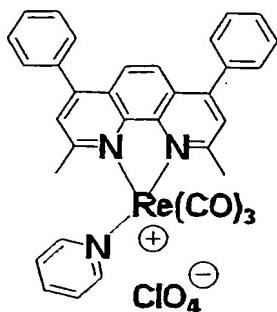


(5)

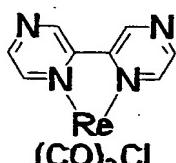
-18-



(6)



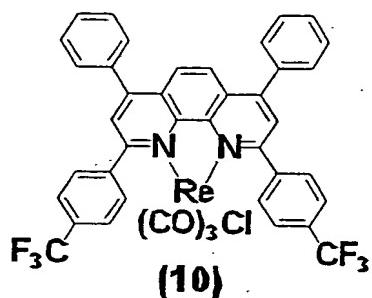
(7)



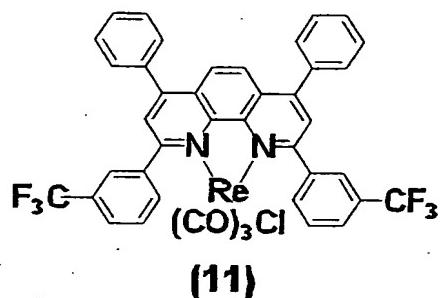
(8)



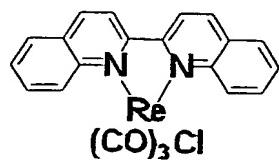
(9)



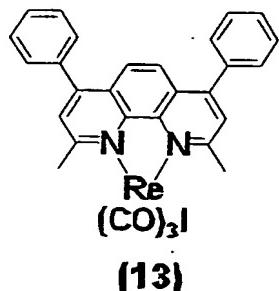
(10)



(11)



(12)



(13)

### Volatility and Stability

Complexes 1 – 3, 11 and 13 were all sublimed under high vacuum at

5 temperatures between 250 and 300 °C. Whilst a small amount of decomposition was observed for all complexes, the elemental analyses and spectroscopic data for the sublimed products are consistent with the formulations given. Complexes 5 and 10 were sublimed at around 275 °C but exhibited decomposition and showed evidence of free ligand (as judged by the <sup>1</sup>H nmr spectra) in the sublimed products.

10 Analysis of the product obtained following the sublimation of complex 6 was consistent with the loss of the 4,4'bpy fragment and the formulation [Re(CO)<sub>3</sub>(Me<sub>4</sub>phen)](CF<sub>3</sub>SO<sub>3</sub>).

An attempt to sublime 7 under high vacuum resulted in complete decomposition of the complex at around 200 °C.

15 Samples of these complexes were left in the solid state under a UV lamp in air for months and no decomposition was observed. However, a sample of 7, on standing as a solid in atmospheric conditions and visible light over a period of weeks, exhibited significant changes in both its absorption and emission spectra.

### 20 Electrochemistry

As mentioned above, aside from altering the substituents, changes to the diimine ligands themselves is another way of altering the LUMO energy, and thus the emission energy, of the Re(I) complexes.

25 Oxidation and reduction potentials were determined for a series of complexes with different diimine ligands and their values compared with bipyridyl and phenanthroline. The results obtained are set out below:

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Complex	Observable redox processes	Oxidation $E_{1/2}$ ( $\Delta E_p$ ) / V	Reduction $E_{1/2}$ ( $\Delta E_p$ ) / V	Solvent
[Re(2,9-Me <sub>2</sub> -4,7-Ph <sub>2</sub> -phen)(CO) <sub>3</sub> Cl] 1	Reversible oxidation and reduction	+1.00 (0.22)	-1.92 (0.22)	CH <sub>2</sub> Cl <sub>2</sub>
[Re(dppt)(CO) <sub>3</sub> Cl] 2	Reversible reduction, irreversible oxidation	$E_{pc} =$ +1.06	-1.35 (0.16)	CH <sub>2</sub> Cl <sub>2</sub>
5 [Re(CO) <sub>3</sub> (2,4,7,9-Ph <sub>4</sub> phen)Cl] 5	Reversible oxidation and reduction	+0.86 V (0.064)	-1.84 V (0.064)	CH <sub>2</sub> Cl <sub>2</sub>
[Re(2,2'-bpz)(CO) <sub>3</sub> Cl] 8	Reversible reduction only	—	-1.23 <sup>(a)</sup> (0.075)	DMF
[Re(2,2'-bpz)(CO) <sub>3</sub> Br] 9	Reversible reduction only	—	-1.23 <sup>(a)</sup> (0.1)	DMF
10 [Re(CO) <sub>3</sub> {2,9-(4-CF <sub>3</sub> Ph) <sub>2</sub> -4,7-Ph <sub>2</sub> phen}Cl] 10	Reversible oxidation and reduction	+0.97 V (0.16)	-1.76V (0.21)	CH <sub>2</sub> Cl <sub>2</sub>
[Re(CO) <sub>3</sub> {2,9-(3-CF <sub>3</sub> Ph) <sub>2</sub> -4,7-Ph <sub>2</sub> phen}Cl] 11	Reversible oxidation and reduction	+0.94 V (0.092)	-1.76V (0.079)	CH <sub>2</sub> Cl <sub>2</sub>
[Re(2,2'-biq)(CO) <sub>3</sub> Cl] 12	Reversible reduction only	—	-1.41 (0.15)	CH <sub>2</sub> Cl <sub>2</sub>

All potentials are quoted relative to Fc/Fc<sup>+</sup> and were recorded in solutions with ~0.2 M [Bu<sup>t</sup>N][PF<sub>6</sub>] as the electrolyte and a scan rate of 0.1 V/s using a glassy carbon working electrode, a platinum auxiliary electrode and a silver wire pseudo reference electrode. For (a) the data is from *Organometallics*, 1996, 236.

Complexes 8 and 9 both show more positive reduction potentials than 1 and are both luminescent although they are very weak both in solution and as solids. The λ<sub>max em</sub> of 9 is 641 nm and it has CIE coordinates of 0.670, 0.329 which is a near-perfect red. The low efficiency of the emissions with bpz ligands has been attributed

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to the basicity of the ligand and the potential for deactivation through interactions at the non-coordinated nitrogen donors (*J. Organometallic Chem.*, 1989, 107).

Complex **2** is a red emitting complex with CIE coordinates in the solid state of  $x = 0.632$  and  $y = 0.366$  with a brightness in the solid state comparable to the red-emitting Ir(III) complex,  $[\text{Ir}(\text{btp})_2(\text{acac})]$ . The emission spectrum of **2** as a solid is shown in Figure 1,  $\lambda_{\text{max em}}$  is 617 nm.

### Device studies

10 Complexes **1**, **2** and **11** have been investigated as emitting materials in EL devices.

Double layer devices with NPD and **1** emit yellow / orange light at a wavelength similar to the solution PL spectrum as shown below in Figure 2.

15 More efficient multi-layer devices were made with complex **1** doped into carbozoyl diphenyl (CBP) at various concentrations. Complex **1** was used in devices with the structure ITO/NPD (50 nm)/**1**: CBP (30 nm)/ BCP (60 nm)/LiF'(1.2 nm)/Al (100 nm). Over the range of doping ratios studied a doping ratio of 1:7 (w/w) proved optimal. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was used as an electron transporting/hole blocking layer. Such a layer is beneficial for improving the 20 efficiency. The best device efficiency was > 6 lm/W and ~ 4 lm/W @ 100 cd/m<sup>2</sup>.

The device characteristics are given in Figure 3.

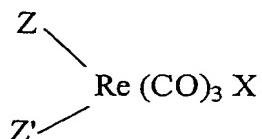
A double layer device with a layer of NPD and a layer of **11** emits red light with CIE coordinates 0.619, 0.371 at 13V.

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CLAIMS

1. An organic electroluminescent device which comprises a compound having a skeleton of the formula:

5

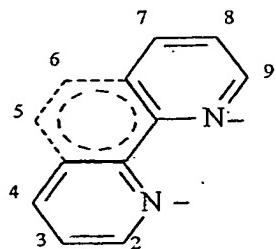


which skeleton can comprise one or more additional aromatic rings, wherein each of Z and Z', which may be the same or different, represents a nitrogen-containing aromatic ring such that the Z and Z' rings either together form a conjugated system, optionally with one or more additional aromatic rings, or at least one of Z and Z'

- 10 form a conjugated system with one or more additional aromatic rings to which Z and Z' is attached, with the proviso that, (a) when the two said rings are pyridyl rings and are connected to one another ortho to the nitrogen atoms then (i) at least one said ring is substituted by at least one electron withdrawing substituent which is a hydrocarbon aryl group or (ii) at least one said ring is fused to another aromatic ring to which the other pyridyl ring is not fused or (iii) the two said rings together form a phenanthroline ring system which is substituted by at least one electron with-drawing substituent which is in the 2, 4, 5, 6, 7 or 9 position, or (b) the two said rings are such that either (i) at least one of them contains at least one further nitrogen atom or (ii) they are fused to another aromatic ring which contains at least one nitrogen atom, and
- 15 X represents an anionic or neutral coligand.

- 20 2. A device according to claim 1 wherein Z and Z' together represent a structure of the formula:-

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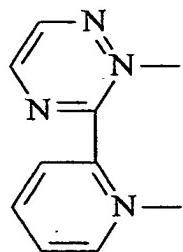


wherein the dotted lines are absent or complete a six membered aromatic ring.

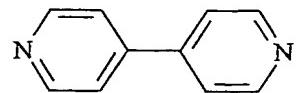
5        3.     A device according to claim 2 wherein the electron withdrawing group is a phenyl group.

4.     A device according to claim 1 wherein the skeleton comprises at least three ring nitrogen atoms which form part of a conjugated system.

5.     A device according to claim 4 wherein Z and Z' together form the  
10    group



6.     A device according to claim 1 wherein Z and Z' both represent



7. A device according to any one of the preceding claims wherein at least one of the rings of the conjugated system possesses at least one electron withdrawing substituent.

8. A device according to claim 7 wherein the electron withdrawing group 5 comprises a nitro; nitroso; cyano; thiocyanato; cyanato; aldehyde; ether; carboxylic acid; azide; aryl; heteroaryl; halogen; ester; chalcogenoester; fluoroalkyl; hypophosphate; sulfonate; acylhalide; amide; substituted N-oxide; hydrazide group; quaternary amine; silyl or substituted, bivalent chalcogenide.

9. A device according to claim 8 wherein the electron withdrawing group 10 is phenyl, 4-pyridyl, pyrazole, furan, thiophene, fluorine, chlorine, bromine, iodine, ethoxycarbonyl,  $\text{CH}_3\text{EO}_2$  or phenyl  $\text{EO}_2$  where E is S, Se or Te, trifluoromethyl, pentafluoroethyl, p-toluene, sulfonate, -CONH<sub>2</sub>, -CONHR or -CONR<sub>2</sub> where R is hydrogen, alkyl or aryl, -NOCH<sub>2</sub>, -NR-NR' where R is as defined above and R<sup>1</sup> is as defined for R, tetraalkylammonium, CH<sub>3</sub>Se or CF<sub>3</sub>S, trifluoromethylphenyl, 15 pentafluoroethylphenyl or pentafluorophenyl group.

10. A device according to any one of the preceding claims wherein X represents an anionic coligand.

11. A device according to any one of the preceding claims wherein the compound possesses a substituent capable of undergoing radical, cationic or anionic 20 polymerisation.

12. A device according to any one of the preceding claims wherein the compound possesses a substituent which forms part of a dendritic structure such that the molecule is a dendrimer.

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13. A device according to any one of claims 1 to 11 wherein the compound possesses an olefin substituent capable of photopolymerisation.

14. A device according to any one of the preceding claims wherein the compound is the light-emitting material in the device.

5 15. A device according to any one of claims 1 to 11 and 14 wherein the compound is Re(CO)<sub>3</sub> 5,6-diphenyl-3-(2-pyridyl)1,2,4-triazinyl Cl.

10 16. A device according to any one of the preceding claims which comprises a transparent substrate layer, a transparent electrode, a layer of light emitting material and a second electrode, said light emitting material comprising said complex.

17. A device according to claim 16 wherein a hole blocking/electron injecting layer is present between the layer of light emitting material and the electrode forming the cathode.

15 18. A device according to any one of the preceding claims wherein the complex is blended with a host material.

19. A device according to claim 1 substantially as hereinbefore described.

20 20. A compound having the skeleton defined in claim 1 which skeleton can comprise one or more additional aromatic rings, each of Z and Z', which may be the same or different, represents a nitrogen-containing aromatic ring such that the Z and Z' rings either together form a conjugated system, optionally with one or more additional aromatic rings or at least one of Z and Z' form a conjugated system with one or more additional aromatic rings to which Z or Z' is attached, with the proviso that the two said rings are such that either (i) at least one of them contains at least one further nitrogen atom or (ii) they are directly fused to another aromatic ring which 25 contains at least one nitrogen atom, and X represents an anionic or neutral coligand, other than Re(CO)<sub>3</sub>[5,6-diphenyl-3-(2-pyridyl)1,2,4-triazinyl]Cl and Re(CO)<sub>3</sub>[3,5,6-tri(2-pyridyl)-1,2,4-triazinyl]Cl.

21. A compound according to claim 18 which has one or more of the features of claims 4 to 13.

30 22. A compound as defined in any one of claims 1 to 15 for use in the manufacture of an electroluminescent device.

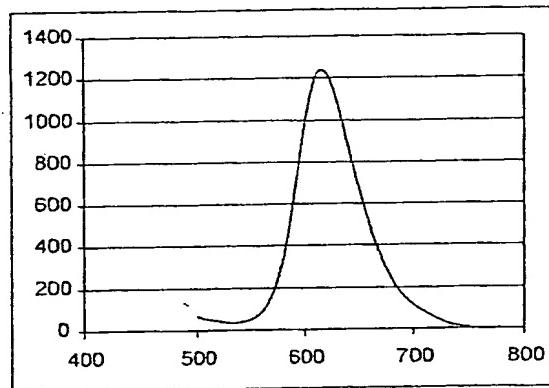


Figure 1

Emission spectra of Re(1) which is  $[\text{Re}(\text{CO})_3(\text{Me}_2\text{Ph}_2\text{phen})\text{Cl}]$   
Normalised emission spectra of  $[\text{Re}(\text{CO})_3(\text{Me}_2\text{Ph}_2\text{phen})\text{Cl}]$

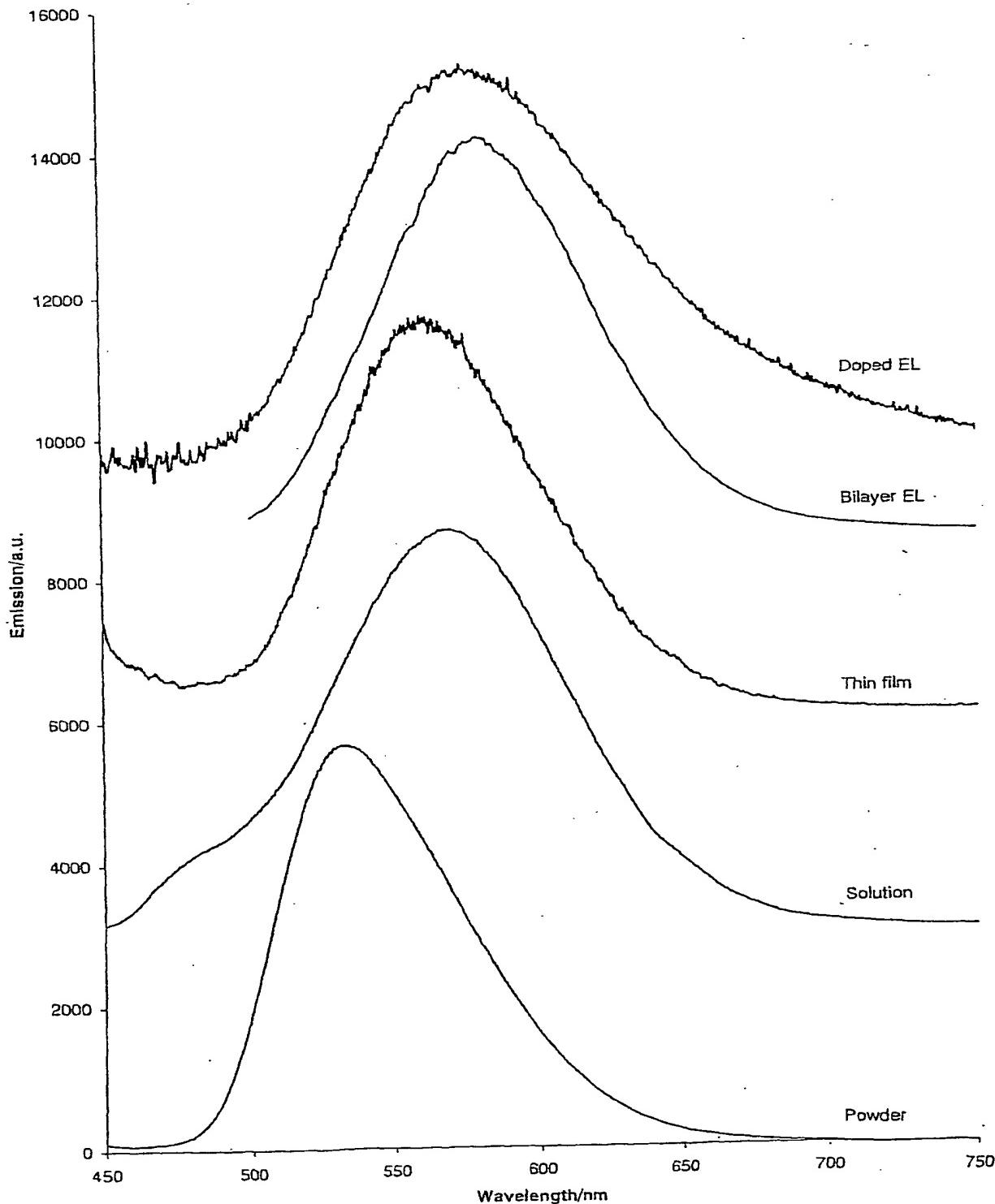


Figure 2

SUBSTITUTE SHEET (RULE 26)

ITO/NPD50nm/Re:CBP(30nm)/BCP60nm/LiF(1.2nm)/Al 100nm

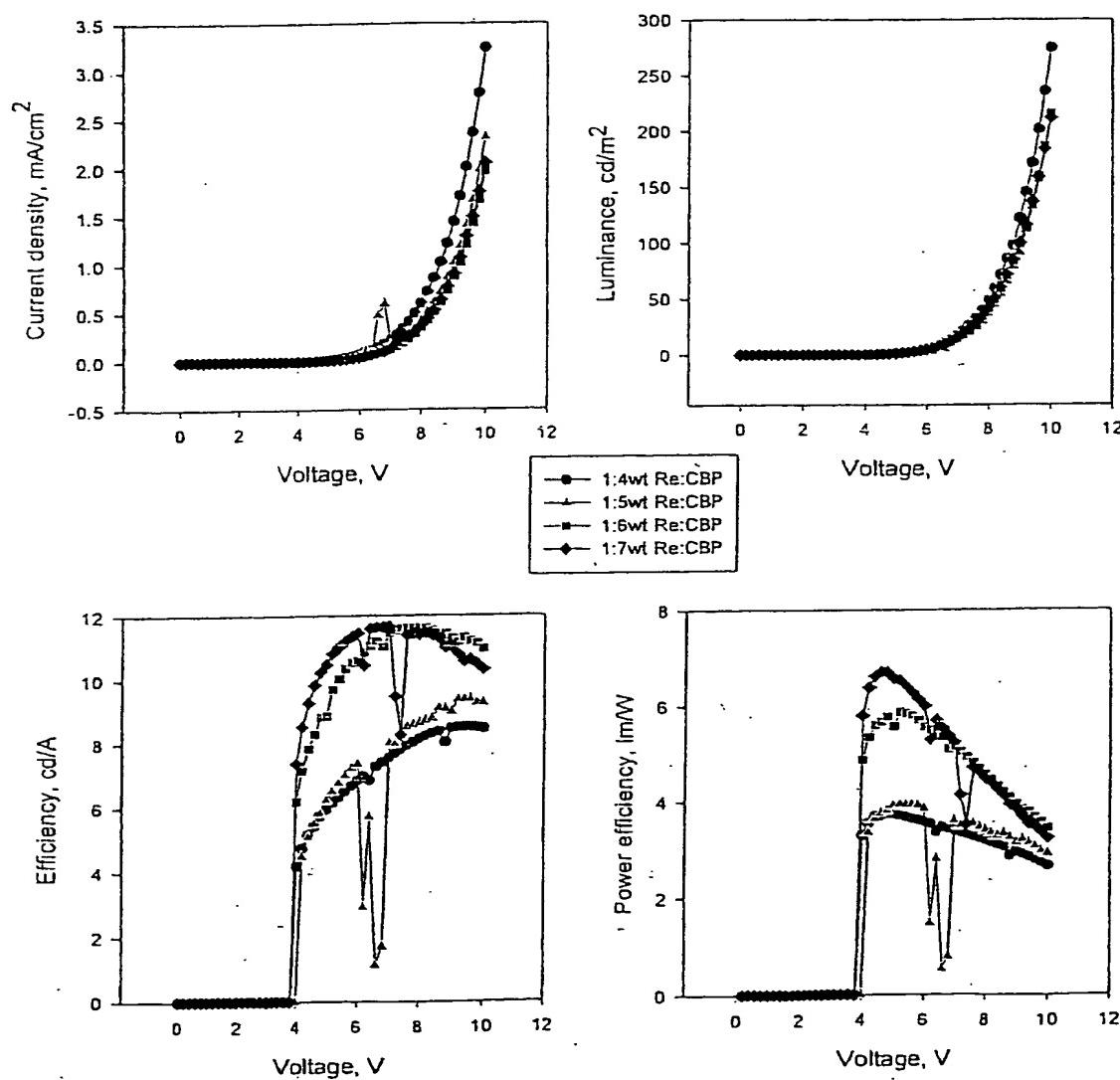


Figure 3

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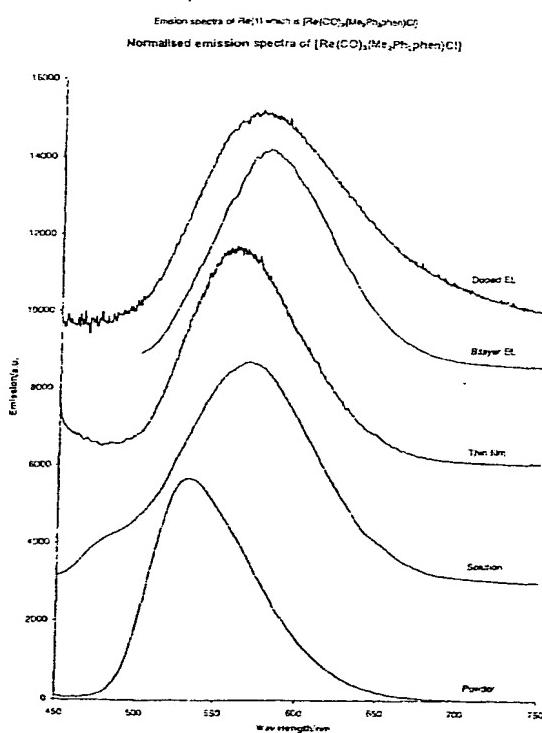
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
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*[Continued on next page]*

(54) Title: RHENIUM COMPOUNDS AND THEIR USE IN ELECTROLUMINESCENT VORRICHTUNGEN



(57) Abstract: An organic electroluminescent device is described which comprises a compound having a skeleton of the formula (I): which skeleton can comprise one or more additional aromatic rings, wherein each of Z and Z', which may be the same or different, represents a nitrogen-containing aromatic ring such that the Z and Z' rings either together form a conjugated system, optionally with one or more additional aromatic rings, or at least one of Z and Z' form a conjugated system with one or more additional aromatic rings to which Z and Z' is attached, with the proviso that, (a) when the two said rings are pyridyl rings and are connected to one another ortho to the nitrogen atoms then (i) at least one said ring is substituted by at least one electron withdrawing substituent which is a hydrocarbon aryl group or (ii) at least one said ring is fused to another aromatic ring to which the other pyridyl ring is not fused or (iii) the two said rings together form a phenanthroline ring system which is substituted by at least one electron withdrawing substituent which is in the 2, 4, 5, 6, 7 or 9 position, or (b) the two said rings are such that either (i) at least one of them contains at least one further nitrogen atom or (ii) they are fused to another aromatic ring which contains at least one nitrogen atom, and X represents an anionic or neutral coligand.



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
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# INTERNATIONAL SEARCH REPORT

International Application No  
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**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09K11/06 H05B33/14 C01G47/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GONG X; NG P K; CHAN W K: "Trifuncional Light-Emitting Molecules Based on Rhenium and Ruthenium Bipyridine Complexes"  <b>ADVANCED MATERIALS</b>,  vol. 10, no. 16, 1998, pages 1337-1340,  XP000785434  the whole document</p> <p style="text-align: center;">----- -/-</p>	1-3, 7-11,14, 16-19,22

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

<p>* Special categories of cited documents :</p> <ul style="list-style-type: none"> <li>*A* document defining the general state of the art which is not considered to be of particular relevance</li> <li>*E* earlier document but published on or after the International filing date</li> <li>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>*O* document referring to an oral disclosure, use, exhibition or other means</li> <li>*P* document published prior to the International filing date but later than the priority date claimed</li> </ul>		<ul style="list-style-type: none"> <li>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>*X* document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</li> <li>*Y* document of particular relevance; the claimed Invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</li> <li>*&amp;* document member of the same patent family</li> </ul>
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Date of the actual completion of the International search	Date of mailing of the International search report
10 July 2003	26.11.2003
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer  Lehnert, A.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 03/01189

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WAI KIN CHAN ET AL: "LIGHT-EMITTING MULTIFUNCTIONAL RHENIUM (I) AND RUTHENIUM (II) 2,2'-BIPYRIDYL COMPLEXES WITH BIPOLAR CHARACTER"            APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, US,            vol. 75, no. 25,            20 December 1999 (1999-12-20), pages 3920-3922, XP000902553            ISSN: 0003-6951            the whole document</p> <p>-----</p>	1-3, 7-11,14, 16-19,22
X	<p>LI Y; WANG Y; ZHANG Y; WU Y; SHEN J: "Carbonyl polypyridyl Re(I) complexes as organic electroluminescent material"            SYNTHETIC METALS,            vol. 99, 1999, pages 257-260, XP002247229            the whole document</p> <p>-----</p>	1-3, 7-11,14, 16-19,22
X	<p>LI Y; LIU Y; GUO J; WU F; TIAN W; LI B;            WANG Y: "Photoluminescent and electroluminescent properties of phenol-pyridine beryllium and carbonyl polypyridyl Re(I) complexes codeposited films"            SYNTHETIC METALS,            vol. 118, 2001, pages 175-179, XP002247230            cited in the application            the whole document</p> <p>-----</p>	1-3, 7-11,14, 16-19,22
X	<p>LUONG J C; NADJO L; WRIGHTON M S: "Ground and Excited State Electron Transfer Processes Involving fac-Tricarbonylchloro(1,10-phenanthroline)-rhenium(I). Electrogenerated Chemiluminescence and Electron Transfer Quenching of the Lowest Excited State"            JOURNAL OF THE AMERICAN CHEMICAL SOCIETY,            vol. 100, no. 18, 1978, - 30 August 1978 (1978-08-30) pages 5790-5795, XP002247231            the whole document</p> <p>-----</p>	1-3, 7-11,14, 16-19,22
A	<p>WO 99 21935 A (SAMUEL IFOR DAVID WILLIAM ; HALIM MOUNIR (GB); ISIS INNOVATION (GB))            6 May 1999 (1999-05-06)            cited in the application            the whole document</p> <p>-----</p>	12

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 03/01189

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 (part), 2, 3, 7 (part) -14 (part), 16 (part), 19 (part), 22 (part)

#### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 (part), 2, 3, 7 (part) -14 (part), 16 (part), 19 (part), 22 (part)

An organic electroluminescent device comprising a rhenium carbonyl compound as disclosed in claims 2 and 3; a rhenium carbonyl compound as defined in claims 2 and 3.

2. claims: 1 (part), 4, 5, 7 (part) -14 (part), 15, 16 (part), 19 (part), 22 (part)

An organic electroluminescent device comprising a rhenium carbonyl compound as disclosed in claims 4 and 5; a rhenium carbonyl compound as defined in claims 4 and 5.

3. claims: 1 (part), 6, 7 (part) -14 (part), 16 (part) - 19 (part), 22 (part)

An organic electroluminescent device comprising a rhenium carbonyl compound as disclosed in claim 6; a rhenium carbonyl compound as defined in claim 6.

4. claims: 20, 21

A rhenium carbonyl compound as defined in claims 20 and 21.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/GB 03/01189

Patent document cited in search report	Publication date		Patent family member(s)		Publication date
WO 9921935	A 06-05-1999	AU	9551598 A		17-05-1999
		CN	1277624 T		20-12-2000
		EP	1027398 A1		16-08-2000
		WO	9921935 A1		06-05-1999
		JP	2001521053 T		06-11-2001
		US	2003165716 A1		04-09-2003
		US	6558818 B1		06-05-2003

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